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Scanning Tunneling Microscopy Studies of Diamond Films and Optoelectronic Materials

Summary Report

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1. INTRODUCTION

In this summary report, we summarize the results of the entire project entitled "Scanning Tunneling Microscopy Studies of Diamond Films and Optoelectronic Materials" from December 1, 1992 to November 30, 1996. The NASA grant number of this project is NAG-1-1468. We present a summary of the research, citations of publications resulting from the research and abstracts of such publications. We have made no inventions in the performance of the work in this project.

The main goals of the project were to set up a chemical vapor deposition (CVD) diamond growth system attached to an ultrahigh vacuum (UHV) atomic resolution scanning tunneling microscopy (STM) system and carry out experiments aimed at studying the properties and growth of diamond films using atomic resolution UHV STM. We successfully achieved these goals. We observed, for the first time, the atomic structure of the surface of CVD grown epitaxial diamond (100) films using UHV STM.¹ We studied the effects of atomic hydrogen on the CVD diamond growth process.² We studied the electronic properties of the diamond (100) (2x1) surface^{1,2} and the effect of alkali metal adsorbates such as Cs on the work function of this surface using UHV STM spectroscopy techniques. We also studied, using STM, new electronic materials such as carbon nanotubes³ and gold nanostructures.⁴ This work resulted in four publications in refereed scientific journals and five publications in refereed conference proceedings.

2. SUMMARY OF RESEARCH

Each epitaxial diamond film used in our studies was grown on a polished 0.25 x 1.5 x 1.5 mm³ (100) type 2b high-pressure, high temperature (HPHT) grown diamond substrate purchased from Harris Corporation. The substrate was cleaned ultrasonically in acetone, and then in a mixture of HCl and HNO₃ (1:3), and rinsed in triple distilled water. Using a hot-tungsten filament CVD reactor, we deposited a conducting diamond film one to two microns thick on the substrate surface. The reactor is coupled to the UHV STM chamber via an all-metal through valve, and the samples are transferred from the reactor to the UHV STM chamber without contamination by exposure to air. We deposited the diamond film for 120 minutes with a substrate temperature of 850 °C at a pressure of 30 Torr using hydrogen and methane with flow rates of 200 standard cubic centimeters per minute (sccm) and 1 sccm, respectively. The tungsten filament temperature was 2200 °C. The growth experiment was stopped by first shutting off only the methane flow and maintaining the sample, filament, and H₂ settings for 2 minutes. The filament was then turned off followed by the sample heater and then the H₂ flow being turned off. We obtained the STM images in UHV at a pressure of 1.0×10^{-10} Torr using an Aris 5000 UHV compatible STM from Burleigh Instruments. The STM probe was constructed of 20 mil tungsten wire and was electrochemically etched in a KOH solution. Tunneling currents of 2.8 nA with a sample bias of -800 mV were used to obtain atomic resolution. Tunneling current versus voltage (*I-V*) spectroscopy in UHV was obtained using the same image scan parameters (current and sample bias) stated previously.

Using UHV STM, as described above, we directly observed a (2x1) surface reconstruction due to dimerization on epitaxial diamond (100) films.¹ We measured the (2x1) unit cell to be $0.51 \pm 0.01 \times 0.25 \pm 0.01$ nm². Moreover, we observed amorphous atomic regions on the (2x1) reconstructed surface. The amorphous regions consist of linear structures surrounded by particles without any order. These regions resemble *sp*² and *sp*³ bonded carbon in amorphous carbon reported

by Cho *et al.*⁵ using STM in air. We also obtained I - V spectra of undoped and boron doped CVD grown epitaxial films in UHV.

In addition, we studied in detail the effects of atomic hydrogen on CVD grown epitaxial diamond (100) films.² Large area UHV STM images showed that after growth these films consist of oriented (100) planes parallel to the substrate surface. Atomic resolution images showed that the surface of the (100) planes is amorphous. After approximately 2 min of exposure to atomic hydrogen at 30 Torr, the surface was observed to consist of a mixture of amorphous regions and (2x1) dimer reconstructed regions. After 5 min of exposure to atomic hydrogen the surface was observed to consist mostly of (2x1) dimer reconstructed regions. These results are in excellent agreement with a recently proposed model for CVD diamond growth that involves the formation of a carburized layer on the diamond substrate that is converted to diamond by atomic hydrogen.⁶

We also studied, using STM in air, the structural and electronic properties of polycrystalline diamond films grown on Si and graphite substrates.⁷ We measured the surface electronic density of states of such films using STM I - V spectroscopy. We studied new electronic materials such as carbon nanotubes³ and gold nanostructures⁴ using STM in air. Using STM I - V spectroscopy, we observed that carbon nanotubes are metallic.³ We also used I - V spectroscopy to fabricate and characterize gold nanostructures on gold substrates.⁴

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3. CITATIONS OF PUBLICATIONS RESULTING FROM THE RESEARCH

Refereed Journals:

1. R.F. Pinizzotto, H. Yang, J.M. Perez, and J.L. Coffey, "The Observation of Silicon Nanocrystals in Siloxene", *J. Appl. Phys.* **75**, 4486 (1994).
2. W. Rivera, J.M. Perez, R.S. Ruoff, D.C. Lorents, R. Malhotra, S. Lim, Y.G. Rho, E.G. Jacobs, and R.F. Pinizzotto, "Scanning Tunneling Microscopy Current-Voltage Characteristics of Carbon Nanotubes", *J. Vac. Sci. Technol. B* **13**, 327 (1995).
3. R.E. Stallcup, A.F. Aviles, and J.M. Perez, "Atomic Resolution Ultrahigh Vacuum Scanning Tunneling Microscopy of Epitaxial Diamond (100) Films", *Appl. Phys. Lett.* **66**, 2331 (1995).
4. R.E. Stallcup, L.M. Villarreal, S.C. Lim, I. Akwani, A.F. Aviles, and J.M. Perez, "Atomic Structure of the Diamond (100) Surface Studied using Scanning Tunneling Microscopy", *J. Vac. Sci. Technol. B* **14**, 929 (1996).

Refereed Conference Proceedings:

1. J.M. Perez, W. Rivera, C. Lin, R.C. Hyer, M. Green, S.C. Sharma, D.R. Chopra, and A.R. Chourasia, "Scanning Tunneling Microscopy of the Structural and Electronic Properties of Chemical Vapor Deposited Diamond Films", in *Atomic Force/Scanning Tunneling Microscopy*, edited by S. Cohen, M. Bray, M. Lightbody (Plenum Press, New York, 1994). pp. 203-210.
2. W. Rivera, J.M. Perez, R.S. Ruoff, D.C. Lorents, R. Malhotra, S. Lim, Y.G. Rho, E.G. Jacobs, and R.F. Pinizzotto, "Scanning Tunneling Microscopy and Spectroscopy of Carbon Nanotubes", in *Atomic Force/Scanning Tunneling Microscopy*, edited by S. Cohen, M. Bray, M. Lightbody (Plenum Press, New York, 1994). pp. 137-142.
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4. R.E. Stallcup, A.F. Aviles, and J.M. Perez, "Atomic Resolution Ultrahigh Vacuum Scanning Tunneling Microscopy of Diamond (100) Epitaxial Films", in *Atomic Force/Scanning Tunneling Microscopy II*, edited S. Cohen (Plenum Press, New York, 1996). pp. 59-64.
5. J.M. Perez and J.L. Large, "Current versus Voltage Characteristics for Deposition and Removal of Gold Nanostructures on a Gold Surface using Scanning Tunneling

Microscopy", in *Atomic Force/Scanning Tunneling Microscopy II*, edited by S. Cohen (Plenum Press, New York, 1996). pp. 233-239.

4. ABSTRACTS OF PUBLICATIONS RESULTING FROM THE RESEARCH

The observation of silicon nanocrystals in siloxene

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We report the direct observation of silicon nanocrystals in unannealed siloxene using high resolution transmission electron microscopy. The microstructure consists of an amorphous matrix plus silicon crystallites with dimensions of a few nanometers. This is additional evidence that the photoluminescence of silicon-based materials is due to quantum confinement.

J. Appl. Phys. **75** (9), 1 May 1994

Scanning tunneling microscopy current-voltage characteristics of carbon nanotubes

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Scanning tunneling microscopy has been used to obtain images and current-voltage (I-V) curves of carbon nanotubes produced by arc discharge of carbon electrodes. The STM I-V curves indicate that carbon nanotubes with diameters from 2.0 to 5.1 nm have a metallic density of states. Using STM, we also observe nanometer-size graphene sheets which are four graphite layers thick. The STM images of carbon nanotubes are in good agreement with transmission electron microscope images.

J. Vac. Sci. Technol B **13**(2), Mar/Apr 1995

Atomic resolution ultrahigh vacuum scanning tunneling microscopy of epitaxial diamond (100) films

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NLB

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We report atomic resolution images of chemical vapor deposition grown epitaxial diamond (100) films obtained in ultrahigh vacuum (UHV) with a scanning tunneling microscope. A (2x1) dimer surface reconstruction and amorphous atomic regions are observed. The (2x1) unit cell is measured to be $0.51 \pm 0.01 \times 0.25 \pm 0.01$ nm². The amorphous regions are identified as amorphous carbon. A radial structure 1.5 nm in diameter is observed on a plane at a 20° slope to the (2X1) surface. Tunneling current versus voltage spectra in UHV and Raman spectra are also obtained.

Appl. Phys. Lett. **66** (18), 1 May 1995

Atomic structure of the diamond (100) surface studied using scanning tunneling microscopy

NLB

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Atomic resolution ultra-high vacuum scanning tunneling microscopy studies of chemical-vapor-deposition-grown epitaxial diamond (100) films are reported. After growth, the surface of the epitaxial films is amorphous at the atomic scale. After 2 min of exposure to atomic hydrogen at 30 Torr, the surface is observed to consist of amorphous regions and (2x1) dimer reconstructed regions. After 5 min of exposure to atomic hydrogen, the surface is observed to consist mostly of (2X1) dimer reconstructed regions. These observations are compared with a recent model for chemical-vapor-deposition diamond growth. Tunneling current versus voltage spectroscopy of undoped and boron-doped epitaxial diamond (100) films is also reported.

J. Vac. Sci. Technol. B **14**(2), Mar/Apr 1996

Scanning tunneling microscopy of the structural and electronic properties of chemical vapor deposited diamond films

NDB

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Abstract: Scanning tunneling microscopy (STM) and spectroscopy have been used to characterize the structural and electronic properties of diamond films grown using hot tungsten filament and microwave plasma chemical vapor deposition. The hot-filament-grown films contained microcrystallites measuring 50 nm, while the microwave-plasma-grown films contained larger crystallites measuring 500 nm. STM tunneling current versus voltage (I-V) curves for the hot-filament-grown films exhibit a zero-current region about the Fermi level corresponding to a surface band gap of 4.1 eV, to be compared with the bulk band gap of diamond of 5.45 eV. The surface electronic density of states computed from these I-V curves is in good agreement with x-ray photoelectron and appearance potential spectroscopies. The I-V curves for the microwave plasma grown films exhibit rectifying behavior in good agreement with a Schottky model for surface band bending.

Atomic Force/Scanning Tunneling Microscopy

Edited by S. Cohen *et al.*, Plenum Press, New York, 1994

NDB

Scanning tunneling microscopy and spectroscopy of carbon nanotubes

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Abstract: Scanning tunneling microscopy (STM) and spectroscopy have been used to obtain images and current-voltage (I-V) curves of carbon nanotubes. The nanotubes are 5-7 nm in diameter

and up to 1 μm in length. The I-V curves indicate that carbon nanotubes with diameters of approximately 5.0 nm are metallic. This observation is consistent with recent theoretical predictions concerning the electronic structure of carbon nanotubes in relation to their diameter and helicity. Using STM, we also observe graphene sheets in the carbon soot that is produced during the arc discharge. The STM images of nanotubes are in good agreement with transmission electron microscopy images. Potential applications of carbon nanotubes include novel nanometer-size electronic devices and fiber-reinforced materials.

Atomic Force/Scanning Tunneling Microscopy

Edited by S. Cohen *et al.*, Plenum Press, New York, 1994

NDP

Scanning tunneling microscopy of chemical vapor deposition diamond film growth on highly-oriented-pyrolytic graphite and Si

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Abstract: We report scanning tunneling microscopy (STM) studies of chemical vapor deposition (CVD) diamond film growth on highly-oriented-pyrolytic graphite (HOPG) and Si. The films were grown using hot-tungsten filament CVD. Using conditions typical for CVD diamond growth, we find that HOPG is etched by atomic hydrogen such that oriented hexagonal pits 5-500 nm in diameter are produced on the surface. Diamond crystallites are observed to nucleate on the walls of these pits and not on the smooth sp^2 bonded parts of the surface. At lower sample temperature, HOPG is etched such that large circular pits approximately 1000 nm in diameter and 0.7 nm deep are produced. Nanoscale linear structures, which we conjecture are hydrocarbon chains, are observed in these pits. These structures orient themselves when a voltage of 10 V is applied to the tip. The initial stages of diamond film growth on Si was studied. Polycrystalline films on Si approximately 2 μm thick were imaged in air from a micron to atomic resolution scale. The micron scale images show that these films consist of diamond crystallites with (100) or (111) oriented faces. Atomic resolution images of the (100) surface in air showed a 2X1 dimer reconstruction with a distance between dimer rows of approximately 5.1 nm.

Atomic Force/Scanning Tunneling Microscopy II

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Atomic resolution ultrahigh vacuum scanning tunneling microscopy of diamond (100) epitaxial films

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Abstract: Atomic resolution images of epitaxial (100) diamond films were obtained in ultrahigh vacuum (UHV) with a scanning tunneling microscope (STM). The dimer row spacing, spacing between dimer pairs in a row, and single atomic step height were measured to be 0.5 nm, 0.25 nm and 0.1 nm, respectively. Different forms of amorphous carbon were also observed in UHV. Some forms appeared to be randomly oriented while others appeared chain-like. A radial reconstruction 1.5 nm in diameter was found on a 20 ° slope to a group of (100) 2x1 reconstructions. Current vs voltage spectra were obtained in UHV and showed the electronic structure of the surface of the film. Raman spectra of the diamond film showed sp^2 and sp^3 carbon peaks.

Atomic Force/Scanning Tunneling Microscopy II
Edited by S. Cohen *et al.*, Plenum Press, New York, 1996

Current versus voltage characteristics for deposition and removal of gold nanostructures on a gold surface using scanning tunneling microscopy

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Abstract: We report the deposition and removal of gold nanostructures 50-200 Å in diameter on a gold surface using scanning tunneling microscopy (STM) by applying a DC voltage to the tip. The DC voltage is applied using tunneling current versus voltage (I-V) spectroscopy. We observe the deposition of a gold nanostructure at a threshold voltage of approximately 2.8 V. The I-V curves show a large current after deposition consistent with a tip-sample connection. We also observe the removal of an existing nanostructure which leaves a pit behind on the surface by applying a DC voltage with the tip directly above the nanostructure. In this case, the I-V curves show no current consistent with no tip-sample connection being formed. We conjecture that an electric-field-induced force picks up the nanostructure in whole onto the tip. We propose that occasional pit formation is the result of a tip-sample connection which breaks while the tip is under bias.

Atomic Force/Scanning Tunneling Microscopy II
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